

Comparative LCA of multi-product processes with non-common products: a systematic approach applied to chlorine electrolysis technologies

Johannes Jung · Niklas von der Assen · André Bardow

Received: 4 July 2011 / Accepted: 7 November 2012 / Published online: 22 November 2012
© Springer-Verlag Berlin Heidelberg 2012

Abstract

Purpose Multi-product processes are one source of multi-functionality causing widely discussed methodological problems within life cycle assessment. A multi-functionality problem exists for comparative life cycle assessment (LCA) of multi-product processes with non-common products. This work develops a systematic workflow for fixing the multi-functionality problem caused by the non-common products. A novel technology for chlor-alkali electrolysis is analyzed and compared to the industrial standard technology to illustrate the approach and to benchmark the new technology's environmental impact.

Methods A matrix-based workflow for comparative LCA of multi-product systems is presented. Products are distinguished in main products and by-products based on the reason of process operation. We argue that only main products form the reference flows of the compared multi-product systems. Fixing the multi-functionality problem follows directly from the chosen reference flows. The framework suggests system expansion to fix the multi-functionality problem if non-common main products exist. Non-common by-products still cause a multi-functionality problem. These by-products are systematically identified and the multi-functionality problem is fixed with avoided burden

and allocation. A case study applies the workflow for comparing environmental impacts of the standard chlorine electrolysis to a novel process using oxygen-depolarized cathodes. Three scenarios are derived and evaluated. The assessed impact categories are cumulative energy demand, global warming potential, acidification potential, photochemical ozone creation potential, eutrophication potential, and human toxicity potential.

Results and discussion The proposed workflow minimizes the methodological choices. The multi-functionality problem is systematically fixed based on the distinction between the main products and by-products. Inconsistent solutions are prevented by rigorous identification of unequal by-products within the compared systems. Selecting avoided burden processes or allocation factors is the remaining ambiguous choice common to the standard methods. The case study demonstrates the applicability of the workflow to comparative LCA of multi-product systems. The case study results show lower environmental impacts for the novel electrolysis technology in all practically relevant scenarios and impact categories.

Conclusions The framework for comparative LCA of multi-product systems with non-common products adds systematic clarity to the general ISO standards. The approach reduces the subjective choices of LCA practitioners to the identification of reason of process operation. This reason is defined if the site-specific economic conditions are known. The matrix-based formulation allows identification of inconsistencies caused by multi-functionality. For the novel electrolysis technology, the results indicate significant potential for environmental impact reduction.

Responsible editor: Liselotte Schebek

Electronic supplementary material The online version of this article (doi:10.1007/s11367-012-0531-7) contains supplementary material, which is available to authorized users.

J. Jung · N. von der Assen · A. Bardow (✉)
Lehrstuhl für Technische Thermodynamik,
RWTH Aachen University, Schinkelstr. 8,
52062 Aachen, Germany
e-mail: andre.bardow@ltt.rwth-aachen.de

Keywords Chlorine electrolysis · Comparative LCA · Industrial processes · Multi-functionality · Multi-product processes

1 Introduction

The environmental impact of products, processes, and services can be analyzed using life cycle assessment (LCA). Environmental impacts are assessed using a functional unit as point of reference. The functional unit is fixed by LCA practitioners during the “goal and scope” phase of a LCA. For comparative LCA, the functional unit has to be carefully defined such that the compared alternatives fulfil an equal function. Severe methodological problems occur as soon as processes have more than one function (e.g., Azapagic and Clift 1999b, 2000). In many cases, the environmental impacts of these multi-functional processes have to be allocated to single functions. In LCA, this is referred to as the multi-functionality or allocation problem (e.g., Heijungs and Guinée 2007; Curran 2007; Finnveden et al. 2009).

The ISO standard for LCA (ISO 2006a, b) provides a general code of practice for fixing the multi-functionality problem. The code of practice suggests a three-step procedure: The first step instructs to avoid allocation by two approaches: Dividing multi-functional processes into sub-processes or expanding the functional unit to include additional functions. The latter procedure is called system expansion. Among others, Ekvall (1999) and Weidema (2001) presented specific guidance on the application of system expansion. Still, allocation cannot always be avoided: Many multi-functional processes cannot be divided into independent sub-processes (e.g., chemical production processes). Expanding the functional unit may conflict with the goal of a study (e.g., environmental impacts of a single product). Therefore, the ISO standard suggests the application of suitable allocation methods in steps 2 and 3. According to step 2, such an allocation method should preferably represent an “underlying physical relationship” between the functions and the environmental impacts. Suitable relationships represent changes in inputs and outputs caused by a change of a single function (Azapagic and Clift 1999a). As a last resort, the third step of the ISO standard suggests allocation based on other relationships between the functions, e.g., economic value. Application of economic allocation has been specified and discussed in several publications (e.g., Frischknecht 1998, 2000; Guinée et al. 2004).

Still, the rather general formulations of the ISO standard (e.g., “wherever possible...”, “where allocation cannot be avoided...”) have been criticized (e.g., Heijungs and Guinée 2007) because they leave a variety of methodological issues unsolved. In her literature review on the multi-functionality problem, Curran (2007) concluded that “the ISO standard should be expanded to provide more precise guidance in how to approach allocation.” In recent years, many authors give more specific guidance to fix the multi-functionality problem (e.g., Suh et al. 2010; Marvuglia et al. 2010).

Moreover, several publications elaborate product-specific allocation procedures, e.g., for bio-fuels (Luo et al. 2009), agricultural products (Svanes et al. 2011), or combined heat and power production (Aldrich et al. 2011).

This work aims at improving the applicability of the ISO standard for the case of comparative LCA of multi-product processes. In literature, multi-product processes are also referred to as multi-output processes (e.g., Curran 2007). Our motivation has its origin in a question raised in the chemical industry: Here, chlorine is mainly produced in the chlor-alkali electrolysis process, which jointly delivers gaseous chlorine, caustic soda in aqueous solution, and gaseous hydrogen as products (Schmittinger et al. 2002). Chlorine production is therefore a popular example for a multi-product process in LCA literature (e.g., Boustead 1994; Frischknecht 1998; Weidema 2001; Schmidt 2009). A new electrolysis technology has recently been developed to reduce 30 % of the electricity demand of the standard electrolysis technology (Moussallem et al. 2008). This new technology uses oxygen-depolarized cathodes (ODC). The ODC process promises a lower electricity demand, but does no longer produce hydrogen. Comparing the ODC process to the existing chlor-alkali electrolysis process reveals a problem for industry and authorities: How are competing processes compared when they produce common (here chlorine and caustic soda) but also non-common products (here hydrogen)? Traditionally, LCA compares products. In LCA, the comparison of processes is therefore reframed as comparison of multi-product systems. Comparing multi-product systems with non-common products raises the question whether the non-common products should be included in the reference flows of the functional unit.

Even with a suitably defined functional unit, a multi-functionality problem remains for the case of non-common products. This can be rigorously shown by the analytical procedure developed by Heijungs and Frischknecht (1998), who studied multi-functionality from a mathematical point of view. They show that not all multi-product processes cause a multi-functionality problem depending on the chosen functional unit. These authors presented a rigorous analytical procedure to identify multi-functional systems that actually cause a multi-functionality problem. The procedure shows that multi-functionality is an intrinsic problem for comparative LCA of multi-product processes with non-common products.

To fix the multi-functionality problem in line with the ISO standard, we propose a systematic framework for comparative LCA of multi-product processes with non-common products. The framework integrates both functional unit definition and fixing the multi-functionality problem. Herein, the procedure from Heijungs and Frischknecht

(1998) is further elaborated to not only identify a multi-functionality problem, but also guide the LCA practitioner to its solution in line with the ISO standard.

The proposed framework is based on the matrix formulation of a LCA (Heijungs and Suh 2002). In Section 2, the fundamentals of this formulation are briefly summarized and the framework is developed. The framework is then applied in Section 3 to compare alternative chlorine electrolysis technologies that have non-common products. This case study is of major current interest to the chemical industry (Moussallem et al. 2009). The problem-specific aim of this work is to investigate the environmental impacts of the ODC process compared to the existing standard process. The results in Section 4 are therefore discussed from two perspectives: applicability of the proposed framework and interpretation of the case study results.

2 Methods

2.1 Problem formulation in matrix representation

LCA of a linear process system can be represented by a set of matrices and vectors. This formulation is comprehensively described by Heijungs and Suh (2002), whose notation is followed here. The next section briefly summarizes the basic fundamentals and highlights the scope of this work.

For a given linear process system, the life cycle inventory (LCI) can be formulated as a set of linear equations defined by the technology matrix \mathbf{A} , the scaling vector \mathbf{s} , and the final demand vector \mathbf{f} :

$$\mathbf{A} \cdot \mathbf{s} = \mathbf{f}. \quad (1)$$

Environmental interventions of a system producing the final demand \mathbf{f} are called LCI results. These results, summarized in a vector \mathbf{g} , are computed from the intervention matrix \mathbf{B} :

$$\mathbf{g} = \mathbf{B} \cdot \mathbf{s}. \quad (2)$$

The technology matrix \mathbf{A} (economic flows) and the intervention matrix \mathbf{B} (environmental flows) characterize a process system and are a result of data collection in LCA studies. The final demand vector \mathbf{f} includes the reference flow of the functional unit. The functional unit is defined in the goal and scope phase of a LCA study. The reference flow may contain one or more economic flows. A scaling vector \mathbf{s} is required to obtain LCI results from Eq. (2); this can be computed for an invertible and positive definite matrix \mathbf{A} :

$$\mathbf{s} = \mathbf{A}^{-1} \cdot \mathbf{f} \Rightarrow \mathbf{g} = \mathbf{B} \cdot \mathbf{A}^{-1} \cdot \mathbf{f}. \quad (3)$$

In comparative LCA, a total number of r product system alternatives are analyzed. The matrices \mathbf{S} , \mathbf{F} , and \mathbf{G} comprise

sets of vectors \mathbf{s} , \mathbf{f} , and \mathbf{g} , respectively, with columns representing the k -th alternative:

$$\mathbf{S} = (\mathbf{s}_1 \mid \dots \mid \mathbf{s}_k \mid \dots \mid \mathbf{s}_r); \quad (4)$$

$$\mathbf{F} = (\mathbf{f}_1 \mid \dots \mid \mathbf{f}_k \mid \dots \mid \mathbf{f}_r);$$

$$\mathbf{G} = (\mathbf{g}_1 \mid \dots \mid \mathbf{g}_k \mid \dots \mid \mathbf{g}_r).$$

$$\mathbf{G} = \mathbf{B} \cdot \mathbf{S} = \mathbf{B} \cdot \mathbf{A}^{-1} \cdot \mathbf{F}. \quad (5)$$

Matrices \mathbf{A} and \mathbf{B} are assumed to contain all possibilities of implemented processes and are thus equal for all alternative product systems. The environmental interventions in \mathbf{G} are aggregated to potential environmental impacts by applying common life cycle impact assessment (LCIA) methods. The LCIA methods are summarized in a characterization matrix \mathbf{Q} . The LCIA results are finally collected in the impact matrix \mathbf{H} :

$$\mathbf{H} = \mathbf{Q} \cdot \mathbf{G} = \mathbf{Q} \cdot \mathbf{B} \cdot \mathbf{A}^{-1} \cdot \mathbf{F}. \quad (6)$$

Multi-functionality is characterized by an over-determined system of linear equations. Such a multi-functional system has a non-square technology matrix \mathbf{A} with more rows (i.e., economic flows) than columns (i.e., processes) and cannot be inverted. A multi-product process is consequently given by a process vector with at least two positive (i.e., output) entries that are seen as useful products (i.e., positive economic value). Computation of LCI results of multi-functional systems requires modifications of the technology matrix \mathbf{A} and the final demand matrix \mathbf{F} (Heijungs and Suh 2002). These modifications represent the procedures for fixing the multi-functionality problem and are commonly denoted system expansion and allocation. However, system expansion can be applied in different variations. In the following, we refer to system expansion only if the functional unit is changed in the final demand matrix \mathbf{F} . For clarity, we distinguish a modification that does not change the functional unit but accounts for multi-functionality with an avoided burden. We refer to this method as avoided burden.

Fixing the multi-functionality problem is not necessary for all non-square technology matrices \mathbf{A} . Heijungs and Frischknecht (1998) presented a method that computes consistent LCI results from Eq. (2) with a non-square matrix \mathbf{A} . The pseudo-inverse matrix \mathbf{A}^+ is used such that the absolute value of a discrepancy vector \mathbf{d} is zero for some final demand vectors \mathbf{f} :

$$\|\mathbf{d}\| = \|\mathbf{A} \cdot \mathbf{A}^+ \cdot \mathbf{f} - \mathbf{f}\| = 0. \quad (7)$$

Heijungs and Frischknecht (1998) concluded that a multi-functionality problem only exists if Eq. (7) is not true.

Recently, the use of the pseudo-inverse matrix \mathbf{A}^+ was further elaborated to compute LCI results using different least-squares techniques (Marvuglia et al. 2010). These authors allowed the discrepancy vector \mathbf{d} to be non-zero and computed LCI results without fixing the multi-functionality problem.

In contrast, this work aims to fix the multi-functionality problem for comparative LCA of multi-product processes with non-common products. The discrepancy vector \mathbf{d} is used to guide LCA practitioners through fixing the multi-functionality problem in line with the ISO standard. Following Heijungs and Frischknecht (1998), the multi-functionality problem is considered to be fixed once the discrepancy vector \mathbf{d} is zero.

For a comparative LCA, the LCI results of multi-functional product systems can be computed from:

$$\mathbf{G} = \mathbf{B} \cdot \mathbf{S} = \mathbf{B} \cdot \mathbf{A}^+ \cdot \mathbf{F}. \quad (8)$$

Here, the LCI results are only consistent if a discrepancy matrix \mathbf{D} was a zero matrix:

$$\mathbf{D}^{m \times r} = (\mathbf{d}_1 \mid \dots \mid \mathbf{d}_r) = \mathbf{A} \cdot \mathbf{A}^+ \cdot \mathbf{F} - \mathbf{F} = \mathbf{0}^{m \times r}. \quad (9)$$

In Eq. (9), the term $\mathbf{A} \cdot \mathbf{A}^+ \cdot \mathbf{F}$ can be considered as a final supply matrix $\tilde{\mathbf{F}}$ (cf. Heijungs and Suh 2002):

$$\tilde{\mathbf{F}} = \mathbf{A} \cdot \mathbf{A}^+ \cdot \mathbf{F}. \quad (10)$$

If the final supply \tilde{F}_{ik} is larger than the final demand F_{ik} , there is an undesired surplus of the i -th product for the k -th system. These undesired surpluses are also identified by positive values for elements $D_{ik} = \tilde{F}_{ik} - F_{ik}$ in the discrepancy matrix \mathbf{D} in Eq. (9). This has also been recognized by Marvuglia et al. (2010, p. 1028).

2.2 Systematic framework for comparative LCA of multi-product processes

A systematic framework for comparative LCA of multi-product systems is shown in Fig. 1. The procedure consists of two stages. In the first stage, the final demand vectors \mathbf{f}_k are defined. In the second stage, the multi-functionality problem is fixed. The discrepancy matrix \mathbf{D} is used to identify the products causing a multi-functionality problem in both stages.

In stage I, the first step of the suggested workflow ensures that the scope of a study is a comparative LCA of alternative multi-product systems. For the case of one multi-product LCA, the approach of Weidema (2001) can be used directly to fix the multi-functionality problem in line with the standard (ISO 2006a). The framework proposed in this work aims at studies where a total number of r multi-product systems are compared. Here, the reference flow typically consists of multiple product flows. A main focus is the case

where multi-product systems have common and non-common products as it is often seen in the chemical industry. Here, the question arises whether the non-common products should be included in the reference flow of the final demand vectors. To answer this question, we suggest distinguishing main products and by-products for the compared multi-product processes. The main products are the site-specific reason of process operation. Remaining products with a positive economic value are called by-products. The reason of process operation has been widely discussed (e.g., Oenning 1997). Similarly, Weidema (2001) uses the term “determining product” for the product that determines the production volume. The distinction between main products and by-products varies depending on site-specific conditions and should always be defined in accordance with economic and technical boundary conditions.

Based on the distinction of main and by-products, we suggest defining a system's function by the main product flows of the compared multi-product processes. Consequently, these main product flows should be used as reference flow in the final demand vectors \mathbf{f}_k . If the non-common products are main products, they should be included in the final demand vector. In this case, the number of main products in the vectors \mathbf{f}_k is unequal, i.e., the multi-product systems have unequal functions. We propose applying system expansion for adjusting the final demand vectors \mathbf{f}_k to include equal numbers of main products. In this situation, allocating environmental impacts only to the common main products is inappropriate from a practical perspective: If the non-common product is a main product, it needs to be produced by all compared multi-product systems. This practical requirement is only captured by system expansion. However, system expansion requires additional processes for the production of the non-common main product. In practice, a total number of q competing processes may be suitable for system expansion. Accounting for all system expansion options increases the original number of r multi-product systems to $(r+q-1)$ system alternatives, so that

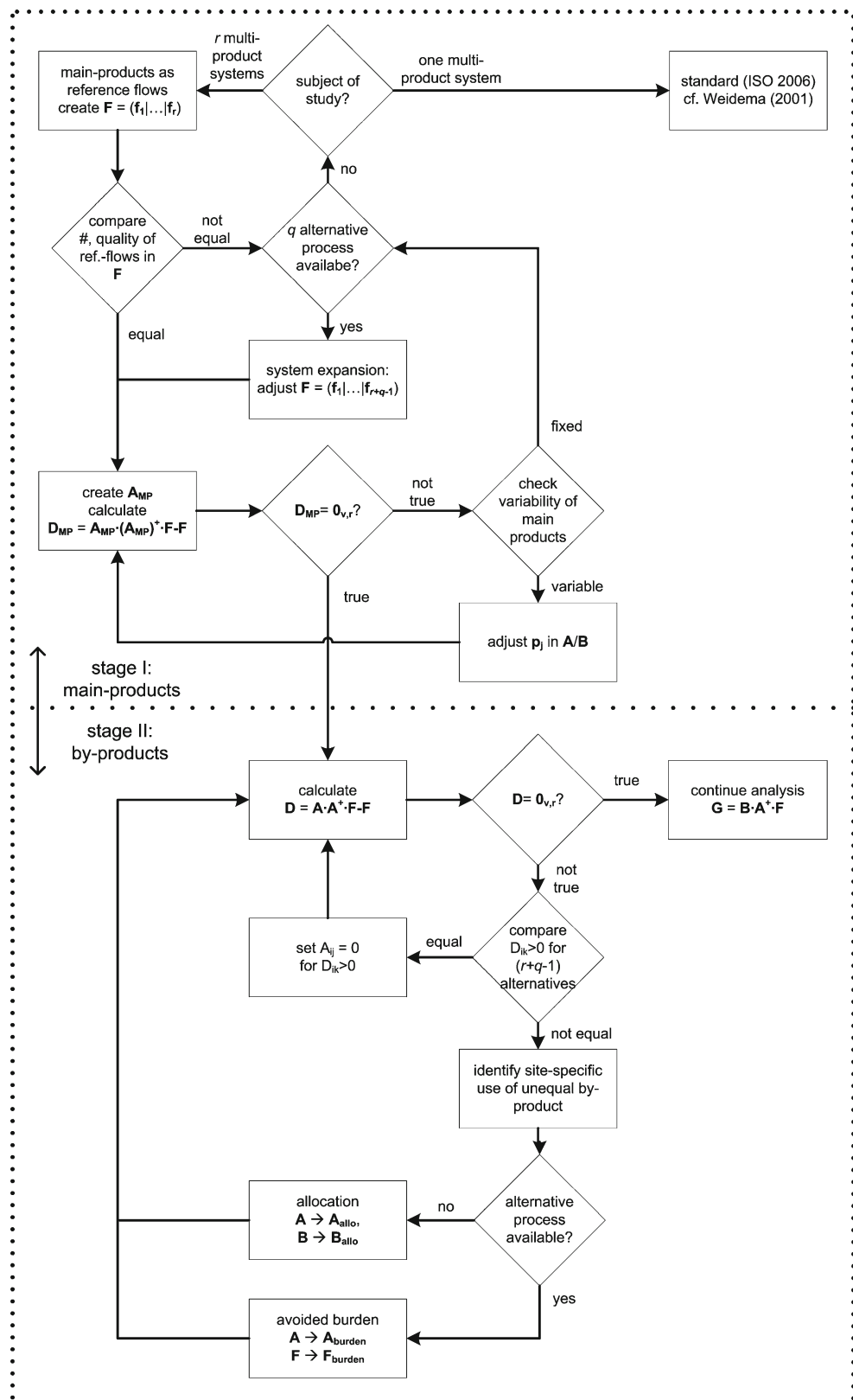
$$\mathbf{F} = (\mathbf{f}_1 \mid \dots \mid \mathbf{f}_{r+q-1}). \quad (11)$$

If a process involved in system expansion is multi-functional, we suggest considering other than the main product(s) as by-products which do not change the final demand matrix \mathbf{F} .

It is possible that a process for system expansion does not exist. In that case, a comparative LCA of alternative multi-product systems is not reasonable because equal main products cannot be delivered. Consequently, the scope of the study has to be reconsidered.

While the compared systems should deliver the same main products after system expansion, comparability is not assured because the main products produced could be

Fig. 1 Systematic workflow for comparative LCA of multi-product processes



supplied in different quantities. It is therefore useful to consider an adjusted technology matrix A_{MP} . The matrix

A_{MP} contains only values for the main products (index MP) while all inputs and outputs other than the main products are

set to zero. A main product discrepancy matrix \mathbf{D}_{MP} can be calculated using the pseudo-inverse \mathbf{A}_{MP}^+ :

$$\mathbf{D}_{MP} = \mathbf{A}_{MP} \cdot \mathbf{A}_{MP}^+ \cdot \mathbf{F} - \mathbf{F}. \quad (12)$$

The matrix \mathbf{D}_{MP} is used to verify that compared process systems deliver the main products in equal quantities. A non-zero discrepancy matrix \mathbf{D}_{MP} reveals unequal main product quantities for the alternative systems. Undesired amounts of a main product are identified by positive discrepancies $(D_{MP})_{ik}$ in the discrepancy matrix \mathbf{D}_{MP} . In this case, the processes delivering the main products have to be analyzed for their flexibility in producing the main products. Flexible production of main products requires an adjustment of the process data in the technology matrix \mathbf{A} and the intervention matrix \mathbf{B} to reflect a change in process operation (e.g., a combined heat and power plant with changing fuel demand and emissions for varying power-to-heat ratios). For the case of fixed production of main products (“joint production,” e.g., processes with fixed stoichiometry), system expansion is again required to adjust the quantities of the main products. Stage I is concluded once a zero discrepancy matrix \mathbf{D}_{MP} is achieved and a set of comparable multi-product systems is established in the final demand matrix \mathbf{F} .

Stage II focuses on by-products of the multi-product systems. By-products may originate from the initial multi-product processes and from multi-functional processes added during system expansion. Non-common by-products can still result in an inconsistent solution of Eq. (8). To avoid an inconsistent solution, stage II continues with calculating the full discrepancy matrix \mathbf{D} to check for a multi-functionality problem:

$$\mathbf{D} = \mathbf{A} \cdot \mathbf{A}^+ \cdot \mathbf{F} - \mathbf{F} = (\mathbf{d}_1 \mid \dots \mid \mathbf{d}_{r+q-1}). \quad (13)$$

If the discrepancy matrix \mathbf{D} is a zero matrix, there is no multi-functionality problem as concluded by Heijungs and Frischknecht (1998) and LCI results are computed consistently using Eq. (8). A non-zero discrepancy matrix \mathbf{D} identifies now a multi-functionality problem caused by unequal by-products. A positive discrepancy D_{ik} marks a by-product (i -th row in \mathbf{D}) and its corresponding multi-product system (k -th column in \mathbf{D}) that needs to be modified to fix the multi-functionality problem.

Before fixing the multi-functionality problem, we suggest identifying the by-product's site-specific use. Based on the site-specific use, the avoided burden method should be applied to account for the by-product surplus. The procedure represents technical reality most adequately (Weidema 2001) and is mathematically described by Heijungs and Suh (2002, p. 41ff).

But avoided burden processes can also be multi-functional. Therefore, recomputing the discrepancy matrix \mathbf{D} is necessary

using the adjusted matrices \mathbf{A}_{burden} and \mathbf{F}_{burden} . The recomputed discrepancy matrix can be used to identify new unequal by-products introduced by the avoided burden process. Using multi-functional avoided burden processes may potentially cause an endless series of loops. An endless loop can be aborted by applying allocation. It is suggested to apply an allocation method once the economic or technical significance of newly introduced by-products is below a certain value. The significance can be checked by comparing LCI results using a suitable allocation factor with LCI results using an allocation factor that neglects the newly introduced by-product (i.e., the by-product has an allocation factor of zero). If the results differ only by a certain threshold value (e.g., max 1 % difference in relevant environmental interventions), then the loop can be aborted.

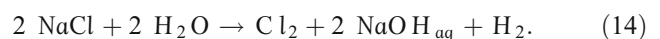
In case an applicable avoided burden process does not exist, it is proposed to use an allocation method according to the ISO standard (ISO 2006b; Azapagic and Clift 1999a; Frischknecht 2000). The mathematical description of the allocation procedure is given by Heijungs and Suh (2002, p. 46ff). Allocation changes both technology matrix \mathbf{A} and intervention matrix \mathbf{B} by splitting columns according to an allocation factor. After allocation, a zero-discrepancy matrix \mathbf{D} can be recalculated using the allocated technology matrix \mathbf{A}_{allo} and consistent LCI results can be computed from Eq. (8) using the allocated technology and intervention matrices \mathbf{A}_{allo} and \mathbf{B}_{allo} .

In the special case of all positive and equal discrepancies D_{ik} in the i -th row, the i -th by-product is produced in equal amounts for all $(r+q-1)$ alternative systems. The surplus of this by-product can therefore be neglected in a comparative LCA. This is achieved by setting the respective process data A_{ij} to zero for all processes. To summarize, the framework illustrated in Fig. 1 provides a systematic two-stage workflow for the comparative LCA of multi-product systems with non-common products.

3 Case study: technology change in chlorine industry

3.1 Chlorine electrolysis technologies

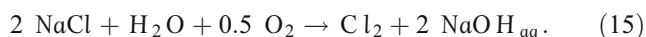
The so-called chlor-alkali electrolysis jointly produces gaseous chlorine, gaseous hydrogen, and an aqueous solution of caustic soda from brine according to the following reaction:



The fundamentals of electrochemistry as well as the existing plant designs are not further elaborated in this work; the interested reader is referred to Schmittinger et al. (2002). The plant design considered as reference technology in this

study is the membrane process. The membrane process is labelled as the Best Available Technique for the chlor-alkali industry by the European Commission (2001) and commonly used for new plants.

A novel promising approach to reduce the electricity demand of the electrolysis process is using ODC (cf. Moussallem et al. 2008). The ODC process is based on a different overall chemical reaction:



This reaction requires 30 % less electricity than reaction (14) (cf. Moussallem et al. 2008). The difference is that hydrogen is not produced and pure oxygen is required as an input. Thus, membrane and ODC processes have only the products chlorine and caustic soda in common. Hydrogen is a non-common product only produced by the membrane process. The framework proposed in Section 2 is therefore applied to a comparative LCA of both technologies.

3.2 System boundaries

The system boundaries for the membrane process system are shown in Fig. 2a. The membrane process delivers gaseous chlorine and hydrogen as well as an aqueous solution of caustic soda of 32 mass percent. A concentration process is included to increase the caustic soda concentration up to the industrial standard concentration of 50 mass percent. Processes for electricity and heat generation are included to supply the energy demand of the electrolysis and the concentration process. Finally, the upstream impact of resource supply, i.e., extraction of NaCl, is included. Figure 2b shows the ODC process system. The ODC process system additionally requires an air fractionation process for oxygen supply. The air fractionation process has nitrogen as a by-product. A steam reforming process is included to account for hydrogen production of the membrane process.

Auxiliary processes such as raw material preparation and product treatment are neglected in this work because data are not yet available for the new ODC process. For the same reason, manufacturing, installation, and deconstruction of the plants are also not considered here. Thus, the case study can be viewed as a simplified “cradle-to-gate” LCA for the products of both electrolysis technologies. The assumptions seem valid for a comparative LCA because the neglected processes and life stages are expected to have similar contributions for both membrane process and ODC process.

3.3 Data sources, software, and impact assessment

The LCA database ecoinvent (2011) contains LCI data for the membrane process. No LCI data are available for the

newly developed ODC process because it is not yet operated on an industrial scale. It is therefore necessary to determine the life cycle inventory data of the electrolysis with a theoretical model. The electricity demand w_{el} of any electrolysis process depends on the voltage U and the specific Faraday constant f according to Faraday's law

$$w_{\text{el}} = \frac{U}{a \cdot f}. \quad (16)$$

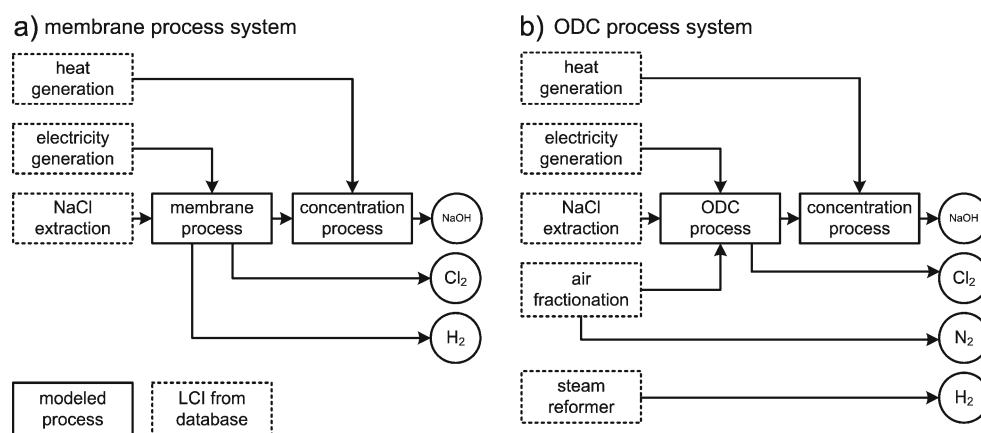
Here, the electrolysis efficiency a accounts for line losses within the electrolysis process. Equation (16) is used to determine the electricity demands of both electrolysis technologies depending on their voltages given in Table 1. The raw material demand is calculated using the stoichiometric reactions given in Eqs. (14) and (15). The heat demand of a concentration process can be calculated from Sattler (2001). The parameters used for modelling are summarized in Table 1.

LCI data from the ecoinvent database for European averages are used for modelling electricity and heat generation as well as NaCl extraction. Hydrogen production from steam reforming and oxygen supply from an air fractionation plant is modelled using LCI data from the GaBi database valid for Germany. The LCI data used for modelling are summarized in Table 2.

All scenarios are modelled using the GaBi software by PE International AG (2011). The impact categories cumulative energy demand (CED), global warming potential (GWP_{100}), acidification potential (AP), photochemical oxidation potential (POCP), eutrophication potential (EP), and human toxicity potential (HTP) are evaluated using the CML characterization factors incorporated in the GaBi software tool.

3.4 Application of the framework

The problem-specific aim of this work is to investigate the environmental impacts the ODC process compared to the membrane process. This is done by applying the framework proposed in Section 2.2. First, the products of both technologies have to be categorized as main and by-products. As indicated in Fig. 2, three possible main products (Cl_2 , NaOH, and H_2) are produced by the membrane process while the ODC process has only two possible main products (Cl_2 and NaOH). The actual main product definition depends on the actual site-specific conditions. In the following section, the framework is demonstrated for three practically relevant scenarios. The scenarios differ in the chosen main products. The scenarios are distinguished by the superscript x of the corresponding final demand matrix \mathbf{F}^x . The superscript x indicates the number of main products in the final demand vectors in Roman numbers. Membrane and

Fig. 2 Process flow sheets for **a** membrane process system and **b** ODC process system

ODC process systems are denoted by indices m and O for the final demand vectors f_k^x , respectively. While the most important matrices are shown here, the [Electronic Supplementary Material](#) provides a detailed list of all matrices used in this work.

The technology matrix **A** is shown in Table 3. It contains the processes shown in Fig. 2. Heat generation and concentration process for NaOH are equal for both electrolysis technologies and therefore not displayed to improve the readability of Table 3.

The numerical values represent the stoichiometric mass relations according to Eqs. (14) and (15). The electricity demands are calculated from Eq. (16) using the parameters listed in Table 1. The matrix displays only the outputs of electricity generation, NaCl extraction, air fractionation, and steam reformer because aggregated LCI data were used to model these processes (cf. Table 2). The environmental impact of the aggregated processes is included in the intervention matrix **B** (not displayed).

Historically, the production of both chlorine and caustic soda has often been the reason of operation of chlor-alkali electrolysis plants. A scenario defining chlorine and caustic soda as main products for both processes appears natural. This leads to a final demand matrix **F^{II}** shown in Table 3. Both alternative systems have an equal number of main products. The calculation of the main product discrepancy matrix **D_{MP}^{II}** from the main product technology matrix **A_{MP}^{II}** yields a zero matrix and thus concludes the main

product stage in the workflow (see Fig. 1), i.e., there are no non-common or unequal main products.

Continuing with the by-product stage, the discrepancy matrix **D^{II}** has two positive entries (Table 4). A surplus of the by-product nitrogen from the air fractionation process that supplies oxygen to the ODC process is indicated by $D_{O,4}^{II} > 0$. The hydrogen surplus from the membrane process is identified by $D_{m,7}^{II} > 0$. The surpluses are handled differently in this example. The steam reformer is used as an avoided burden process for hydrogen production. The nitrogen surplus is treated by allocation because this example assumes that a nitrogen production process suitable for avoided burden does not exist. In fact, the LCI dataset for oxygen supply (cf. Table 2) is already allocated, so a manual allocation is not necessary. A recalculation of the discrepancy matrix **D^{II}** using the adjusted technology and final demand matrices finally yields a zero matrix and allows a consistent computation of LCI results.

A second scenario for defining the main products includes hydrogen as a third main product of the membrane process (cf. **F^{III}** in Table 3). This is especially relevant if hydrogen is required as a chemical and not available otherwise on the site of the chlor-alkali plant. The ODC process does not produce hydrogen. To establish comparability, the final demand vector of the ODC process system has to be expanded for hydrogen from the steam reformer (cf. **f_O^{III}** in Table 3). After system expansion, the main product discrepancy matrix **D_{MP}^{III}** is a zero matrix. The main products can be produced with equal quantities because the steam reformer process is scaled to the stoichiometrically fixed hydrogen production of the membrane process. The full discrepancy matrix **D^{III}** in Table 4 yields only one positive value for $D_{O,4}^{III}$. The nitrogen surplus is treated by allocation as described above in scenario **F^{II}** before the LCI results can be computed.

Electrolysis plants are traditionally built at the location of a chlorine demand. In contrast, caustic soda is often transported to its place of use or stored if there is no demand. Therefore, the last scenario considers only chlorine as a

Table 1 Parameters used in modelling the electrolysis processes

Parameter	Name	Unit	Value
U	Membrane process voltage	V	3.0
U	ODC process voltage	V	2.0
a	Electrolysis efficiency	—	0.97
f	Faraday constant for Cl_2	$(\text{V} \cdot \text{kg}_{\text{Cl}_2})/\text{kWh}$	1.3226

Table 2 Aggregated datasets used for upstream processes (cf. Fig. 2)

Process	Dataset
Electricity generation	Ecoinvent: electricity, medium voltage, production mix, at grid (RER)
NaCl extraction	Ecoinvent: sodium chloride, powder, at plant (RER)
Heat generation	Ecoinvent: steam, for chemical processes, at plant (RER)
Air fractionation	GaBi-PE: oxygen, gaseous, from Linde process (DE)
Steam reformer	GaBi-PE: hydrogen, gaseous, from steam reformer (DE)

RER: Europe; DE: Deutschland (Germany)

main product. This example could also be assessed using the framework of Weidema (2001); however, it is examined here to demonstrate the flexibility of the suggested approach. The final demand matrix \mathbf{F}^I of this scenario is shown in Table 3. A single main product for both alternative systems yields a zero main product discrepancy matrix \mathbf{D}_{MP}^I . In the by-product stage, the full discrepancy matrix \mathbf{D}^I in Table 4 shows positive values for $D_{O,4}^I$ and $D_{m,7}^I$. These values indicate surpluses of nitrogen and hydrogen as already seen in scenario \mathbf{F}^{II} above. Additionally, $D_{m,6}^I > 0$ and $D_{O,9}^I > 0$ identify the surplus of NaOH in both alternative systems. The example in this work assumes an avoided burden process for NaOH does not exist. Therefore, allocation is applied to both electrolysis processes and the air fractionation process before a zero discrepancy matrix \mathbf{D}^I is found. In this example, we apply allocation based on the mass fraction of the products. However, the allocation method choice for chlor-alkali electrolysis is another discussion itself (cf. Boustead 1994) which is not further elaborated here. The [Electronic Supplementary Material](#) provides a brief discussion and results for alternative allocation methods.

4 Results and discussion

4.1 Results

Table 5 summarizes the differences of the membrane (index m) and ODC (index O) process systems for six environmental impact categories h_z . The results are presented relative to the membrane process system illustrating the potential of the ODC process to reduce environmental impacts.

For model validation, the results of the membrane process system were cross-checked with existing LCA data provided in the ecoinvent database. The results are in good agreement for the modelled life phases if the electricity demand used in the model of this work is adjusted to the ecoinvent dataset. The discrepancy of approx. 5 % between the data shown in this work and the ecoinvent dataset corresponds to the contribution from the following life cycle phases: raw material preparation, product treatment, transportation, and plant manufacturing processes. These life stages are neglected in this work (cf. Section 3.2) but included in the ecoinvent dataset.

Table 3 Technology matrix \mathbf{A} and possible final demand matrices \mathbf{F}^I , \mathbf{F}^{II} , and \mathbf{F}^{III} for chlorine production scenarios

Row	Flow	Unit	A							\mathbf{F}^I		\mathbf{F}^{II}		\mathbf{F}^{III}	
										Cl ₂		Cl ₂ , NaOH		Cl ₂ , NaOH, H ₂	
				Electricity generation	NaCl extraction	Air fractionation	Membrane process	ODC process	Steam reformer	f_m^I	f_O^I	f_m^{II}	f_O^{II}	f_m^{III}	f_O^{III}
1	electricity	kWh	1	0	0	−2.34	−1.56	0	0	0	0	0	0	0	0
2	NaCl	kg	0	1	0	−1.65	−1.65	0	0	0	0	0	0	0	0
3	O ₂ , air fractionation	kg	0	0	1	0	−0.23	0	0	0	0	0	0	0	0
4	N ₂ , air fractionation	kg	0	0	3.35	0	0	0	0	0	0	0	0	0	0
5	Cl ₂ , membrane	kg	0	0	0	1	0	0	0	1	0	1	0	1	0
6	NaOH _{membrane}	kg	0	0	0	1.13	0	0	0	0	0	1.13	0	1.13	0
7	H ₂ , membrane	kg	0	0	0	0.03	0	0	0	0	0	0	0	0.03	0
8	Cl ₂ , ODC	kg	0	0	0	0	1	0	0	0	1	0	1	0	1
9	NaOH _{ODC}	kg	0	0	0	0	1.13	0	0	0	0	1.13	0	1.13	0
10	H ₂ , steam reformer	kg	0	0	0	0	0	1	0	0	0	0	0	0	0.03

Heat generation and concentration process for NaOH are equal for both electrolysis technologies and therefore not displayed

Table 4 Full discrepancy matrices **D^I**, **D^{II}**, and **D^{III}** for the different main product scenarios

Row	Flow	Unit	D^I		D^{II}		D^{III}	
			d_m^I	d_O^I	d_m^{II}	d_O^{II}	d_m^{III}	d_O^{III}
1	Electricity	MWh	0	0	0	0	0	0
2	NaCl	kg	0	0	0	0	0	0
3	O ₂ , air fractionation	kg	0	−0.09	0	−0.21	0	−0.21
4	N ₂ , air fractionation	kg	0	0.03	0	0.06	0	0.06
5	Cl ₂ , membrane	kg	−0.56	0	0	0	0	0
6	NaOH _{membrane}	kg	0.50	0	0	0	0	0
7	H ₂ , membrane	kg	0.01	0	0.03	0	0	0
8	Cl ₂ , ODC	kg	0	−0.57	0	0	0	−0.02
9	NaOH _{ODC}	kg	0	0.49	0	−0.02	0	−0.02
10	H ₂ , steam reformer	kg	0	0	0	−0.02	0	0

4.2 Discussion of case study results

The ODC process system has lower environmental impacts in all assessed impact categories for the scenarios **F^I**, **F^{II}**, and **F^{III}** (cf. Table 5). The environmental impact reduction potential of the ODC process system correlates strongly with the CED reduction potentials in all five assessed impact categories: The coefficient of determination R^2 ranges from 0.90 (HTP) to 0.99 (GWP₁₀₀) for the relative impact reduction of the ODC process system. The high level of correlation can be explained by the significant contribution of energy supply to the assessed impacts: The models in this work use the energy demand of the electrolysis processes and the concentration process exclusively to assess their environmental impact. The correlation with CED is not as strong for the HTP impact category. This impact category is more sensitive to the release of toxic substances which is minimized in large-scale energy supply systems. A comprehensive discussion of the generally observed correlation between CED and single-score LCIA indicators was recently presented by Huijbregts et al. (2010). The GWP reduction potential increases if an electricity mix with a higher GWP value is assumed. The steam reformer process does not depend on electricity generation; its relative

contribution to the GWP thus decreases for electricity mixes with higher GWP values.

The ODC process system leads to significantly larger reductions of relative impacts in the AP and POCP categories. For these categories, the reduction potentials are larger than 15 % for both multiple main product scenarios **F^{II}** and **F^{III}**. In this case, the steam reformer process contributes only marginally to both impact categories.

The presented results disregard direct emissions from the electrolysis plant that can have a significant influence particularly in the HTP category. Neglecting this effect is justified in the comparison of membrane and ODC processes at the present stage because no data are yet available for the ODC process. The development of the ODC process plant is aimed at reducing emissions compared to the existing membrane process; thus, the result of the comparison should remain equal if these data are added.

The contribution of auxiliary materials, NaCl preparation, transport and plant manufacturing, and recycling is also neglected in this work due to missing data for the ODC process. The environmental impacts of these items are expected to remain equal for both alternatives and should therefore not strongly influence the result of the comparison.

Table 5 Relative impact difference of membrane and ODC process system comparison using main product scenarios **F^I**, **F^{II}**, and **F^{III}**

	F^I Main product: Cl ₂ ; allocation: mass $\frac{h_{z,O}^I - h_{z,m}^I}{h_{z,m}^I}$	F^{II} Main products: Cl ₂ and NaOH; burden: steam reformer $\frac{h_{z,O}^{II} - h_{z,m}^{II}}{h_{z,m}^{II}}$	F^{III} Main products: Cl ₂ , NaOH, and H ₂ ; expansion: steam reformer $\frac{h_{z,O}^{III} - h_{z,m}^{III}}{h_{z,m}^{III}}$
CED	−24 %	−9 %	−8 %
GWP ₁₀₀	−22 %	−3 %	−3 %
AP	−24 %	−20 %	−19 %
POCP	−21 %	−16 %	−15 %
EP	−17 %	−14 %	−14 %
HTP	−10 %	−11 %	−11 %

The manufacturing and recycling of the plants might have an influence on the comparison because the ODC process plant is manufactured using different materials than a membrane plant. Manufacturing and recycling of the plant should be investigated in the future. However, it is expected that the manufacturing process of the plant does not significantly change the results: Existing data for the membrane process show contributions of only around 5 % in the assessed impact categories for this life stage (ecoinvent 2011).

4.3 Discussion of systematic framework

The case study demonstrates the advantage of the proposed framework: The methodological choices during a comparative LCA of multi-product systems are reduced to distinguishing between the main products and by-products. This classification of main products and by-products can be seen as the question for the reason of process operation or the determining products (cf. Weidema 2001). Once such a classification is made, proper final demand vectors can be derived and existing methods for fixing the multi-functionality problem can be applied. These methods, namely system expansion, avoided burden, and allocation, naturally include further choices. Though the proposed framework cannot remove these choices themselves, it clearly indicates which method to use at a given point in the assessment.

The benefit of the presented framework grows with increasing process integration (i.e., more by-product use) in future process systems. The integration of by-products often varies for different production sites. Therefore, the distinction of main and by-products also depends on site-specific boundary conditions. The framework therefore represents a systematic step towards a site-specific application of LCA for comparative LCA.

The application of the framework to the case study provides a comprehensive view of the proposed methodology. Comparing electrolysis technologies may require choices for processes used for system expansion or avoided burden (e.g., steam reformer for H₂ production). Selecting from competing processes can be complicated and depends highly on the site-specific boundary conditions. The decision for a process used for both system expansion or avoided burden should thus be made in accordance with the scope of the study. For a site-specific assessment, the best available technology for the given site should be chosen.

Multi-functional processes used as avoided burden may potentially cause an endless loop (cf. Fig. 1). As long as avoided burden processes of by-products are multi-functional themselves, choices for either allocation or new avoided burden processes are unavoidable. A rational termination criterion has to be applied, e.g., as proposed at the end of Section 2.2.

The proposed framework prefers system expansion and avoided burden over the application of allocation methods in line with the ISO standard. Even though all methods introduce uncertainty due to the number of possible choices (allocation factors, process selection), system expansion is closer to industrial reality. For comparative LCA, an alternative process will always be searched: an integrated production site would not replace a process as long as there are no alternative processes replacing possibly missing main products or by-products, even though an allocation-based study might advise them to do so.

5 Conclusions and recommendations

The presented work addresses the comparative LCA of multi-product systems, where alternative multi-product processes have common and non-common products. The proposed framework represents a systematic approach that links the functional unit definition to existing methods for fixing the multi-functionality problem. The final demand vector definition is reduced to the reason of process operation. This reason is usually given by economic boundary conditions and forms the basis for distinguishing main products and by-products. Hence, the final demand matrix is not an arbitrary choice, but rather a consequence of the scope of the study and site-specific economic conditions.

Once the final demand matrix has been defined, the framework provides systematic guidance for fixing the multi-functionality problem. System expansion and avoided burden represent industrial reality better than applying allocation methods. The framework therefore proposes to either expand the functional unit (main product) or introduce an avoided burden (by-product). Allocation is applicable for by-products whenever reasonable avoided burdens are not available. The proposed framework does not allow an arbitrary choice between avoided burden and allocation. The choices of the LCA practitioner are limited to choosing either suitable avoided burden processes or allocation factors. The framework adds systematic clarity to the general formulation of the ISO standard focusing on comparative LCA of industrial multi-product systems.

The presented work also points to future research in the field of multi-functionality in LCA. Possibly endless loops may occur whenever avoided burdens are multi-functional processes. The number of multi-functional processes is expected to increase in the future due to industrial development towards higher integration of material and energy flows. The presented methodology proposes a systematic approach to handle these loops. The proposed cut-off/allocation criterion should be further systematized in a mathematical approach to apply LCA to the design and optimization of future process systems. A promising approach in this direction was recently given by Marvuglia et al. (2010).

The results obtained in the case study show lower environmental impacts for the ODC process system in most scenarios and impact categories. To further strengthen the validity of these outcomes, the influence of direct plant emissions and plant manufacturing needs to be included in a next step as soon as data are available for the ODC process. The data in this work show already significant potential for the ODC technology to reduce the environmental impacts of the chlor-alkali industry.

Acknowledgments This work has been carried out within the project “CO₂ Reduction during the Production of Basic Chemicals” (01LS05013). The project is funded by the German Federal Ministry of Education and Research (BMBF) within the funding priority “Research for Climate Protection and Protection from Climate Impacts.” The authors would like to thank two anonymous reviewers for their valuable comments and recommendations that significantly helped to improve this work. The authors would also like to thank Scott Johnson, Matt Brunner, and Andreas Peters for their helpful comments on the preparation of the material.

References

- Aldrich R, Llauró FX, Puig J, Mutjé P, Àngels Pàlach M (2011) Allocation of GHG emissions in combined heat and power systems: a new proposal for considering inefficiencies of the system. *J Cleaner Prod* 19(9):1072–1079
- Azapagic A, Clift R (1999a) Allocation of environmental burdens in multiple-function systems. *J Cleaner Prod* 7(2):101–119
- Azapagic A, Clift R (1999b) Allocation of environmental burdens in co-product systems: product-related burdens (part 1). *Int J Life Cycle Assess* 4(6):357–369
- Azapagic A, Clift R (2000) Allocation of environmental burdens in co-product systems: process and product-related burdens (part 2). *Int J Life Cycle Assess* 5(1):31–36
- Boustead I (1994) Report 5: Co-product allocation in chlorine plants. In: *Eco-profiles of the European polymer industry*. Association of European Plastics Manufacturers (APME), Brussels
- Curran MA (2007) Co-product and input allocation for creating life cycle inventory data: a literature review. *Int J Life Cycle Assess* 12:65–78
- Ecoinvent (2011) Swiss Centre for Life Cycle Inventories. <http://www.ecoinvent.ch>. Accessed 6 Apr 2011
- Ekvall T (1999) System expansion and allocation in life cycle assessment. PhD thesis. Chalmers University of Technology, Sweden
- European Commission (2001) Reference Document on Best Available Techniques in Chlor-Alkali Manufacturing Industry. Integrated Pollution Prevention and Control (IPPC). Available online: <http://eippcb.jrc.es/reference/>. Accessed 23 Mar 2011
- Finnveden G, Hauschild MZ, Ekvall T, Guinée J, Heijungs R, Hellweg S, Koehler A, Pennington D, Suh S (2009) Recent developments in life cycle assessment. *J Environ Manage* 91(1):1–21
- Frischknecht R (1998) Life Cycle Inventory for decision-making—scope dependent inventory system models and context-specific joint product allocation. Ph.D. Thesis. Swiss Federal Institute of Technology, Zurich
- Frischknecht R (2000) Allocation in life cycle inventory analysis for joint production. *Int J Life Cycle Assess* 5(2):85–95
- Guinée J, Heijungs R, Huppes G (2004) Economic allocation: examples and derived decision tree. *Int J Life Cycle Assess* 9(1):23–33
- Huijbregts MAJ, Hellweg S, Frischknecht R, Hendriks HWM, Hungerbühler K, Hendriks AJ (2010) Cumulative energy demand for predictor for the environmental burden of commodity production. *Environ Sci Technol* 44(6):2189–2196
- Heijungs R, Frischknecht R (1998) A special view on the nature of the allocation problem. *Int J Life Cycle Assess* 3(6):321–332
- Heijungs R, Guinée JB (2007) Allocation and ‘what-if’ scenarios in life cycle assessment of waste management systems. *Waste Manage* 27(8):997–1005
- Heijungs R, Suh S (2002) The computational structure of life cycle assessment. Kluwer, Dordrecht
- ISO Norm 14040 (2006a) Environmental management—life cycle assessment—principles and framework. Geneva, Switzerland: International Organization for Standardization
- ISO Norm 14044 (2006b) Environmental management—life cycle assessment—requirement and guidelines. Geneva, Switzerland: International Organization for Standardization
- Luo L, van der Voet E, Huppes G, de Haes HAU (2009) Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol. *Int J Life Cycle Assess* 14(6):529–539
- Marvuglia A, Cellura M, Heijungs R (2010) Toward a solution of allocation in life cycle inventories: the use of least-squares techniques. *Int J Life Cycle Assess* 15(9):1020–1040
- Moussallem I, Jörisen J, Kunz U, Pinnow S, Turek T (2008) Chlor-alkali electrolysis with oxygen depolarized cathodes: history, present status and future prospects. *J Appl Electrochem* 38(9):1177–1194
- Moussallem I, Pinnow S, Turek T (2009) Möglichkeiten zur Energierückgewinnung aus Wasserstoff bei der Chlor-Alkali-Elektrolyse. *Chem Ing Tech* 81:489–493
- Oenning A (1997) Theorie betrieblicher Kuppelproduktion. Ph.D. Thesis. RWTH Aachen University (in German)
- PE International AG (2011) <http://www.pe-international.com>. Accessed 4 Apr 2011
- Sattler K (2001) Lösungseindampfung (in German), Thermische Trennverfahren, 3rd edn. Wiley, New York, pp 617–676
- Schmidt M (2009) Die Ökobilanzierung vor dem Hintergrund der Nutzenmaximierung (in German). In: Feifel S, Walk W, Wursthorn S, Schebek L (eds) *Ökobilanzierung 2009—Ansätze und Weiterentwicklungen zur Operationalisierung von Nachhaltigkeit*. pp 21–37
- Schmittinger P et al. (2002) Chlorine. In: *Ullmann's encyclopedia of industrial chemistry*, 6th edn. Wiley, New York, pp 399–481
- Suh S, Weidema BP, Heijrup J, Heijungs R (2010) Generalized make and use framework for allocation in life cycle assessment. *J Ind Ecol* 14(2):335–353
- Svanes E, Vold M, Hanssen O (2011) Effect of different allocation methods on LCA results of products from wild-caught fish and on the use of such results. *Int J Life Cycle Assess* 16(6):512–521
- Weidema BP (2001) Avoiding co-product allocation in life cycle assessment. *J Ind Ecol* 4(3):11–33